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WO 97/25129 A1 WO 96/01683 A1
WPI Abstract Accession No. 1998-182373 & JP
100036114 A WPI Abstract Accession No. 1998-182372
& JP 100036113 A

(58) Field of Search

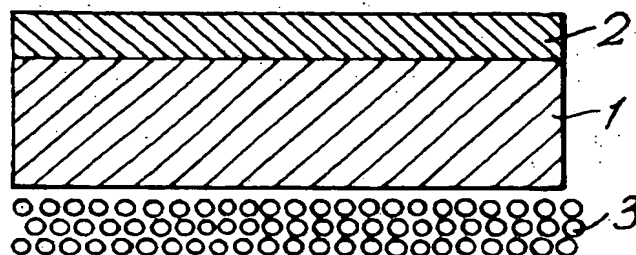
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(54) Abstract Title

Molecular sieve compositions

(57) A molecular sieve composition, and process of manufacture, comprising a permselective layer (2, Figure 1) of dense, columnar, polycrystalline molecular sieve material and a second independently selected layer of polycrystalline molecular sieve material (3, Figure 1) having a surface in contact with that of the permselective layer (2, Figure 1). Also disclosed is a molecular sieve membrane composite composition comprising a permselective layer 2 of dense, columnar, polycrystalline molecular sieve material deposited on a substrate 1 and a catalytically active region 3 which is not in direct contact with the permselective layer 2. Preferably the molecular sieve material is selected from the group consisting of molecular sieve X, Y, ZSM-5, silicalite and mixtures thereof. Preferably the substrate is selected from a group consisting of stainless steel and alumina substrates and the catalyst is a xylene isomerisation catalyst.

Fig.11.



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Fig.1.

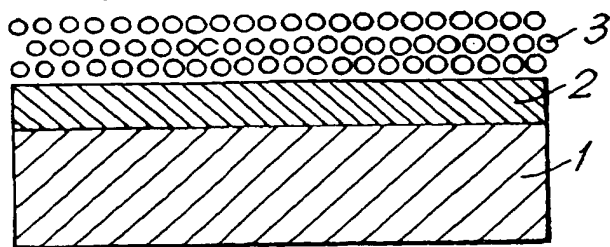


Fig.2.

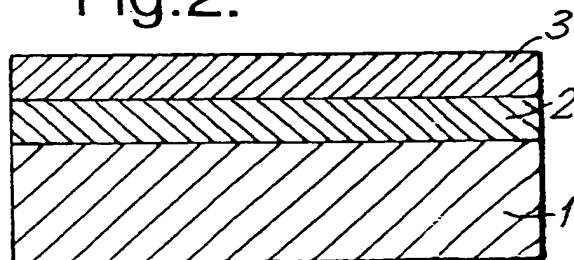


Fig.3.

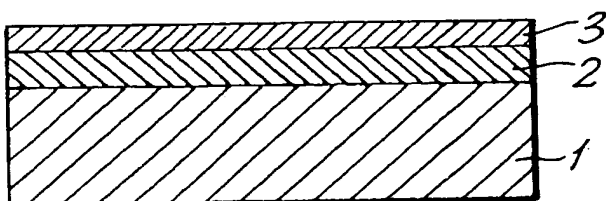


Fig.4.

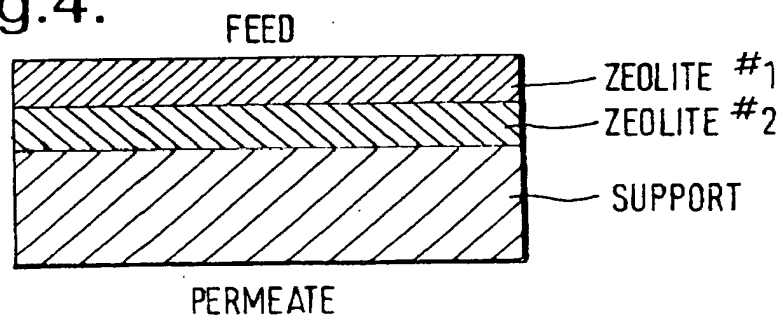


Fig.5.

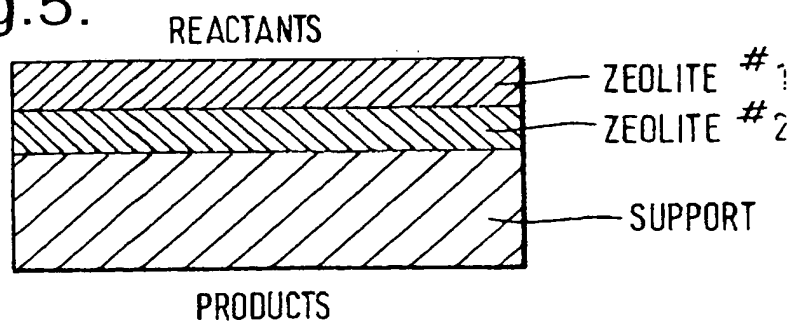


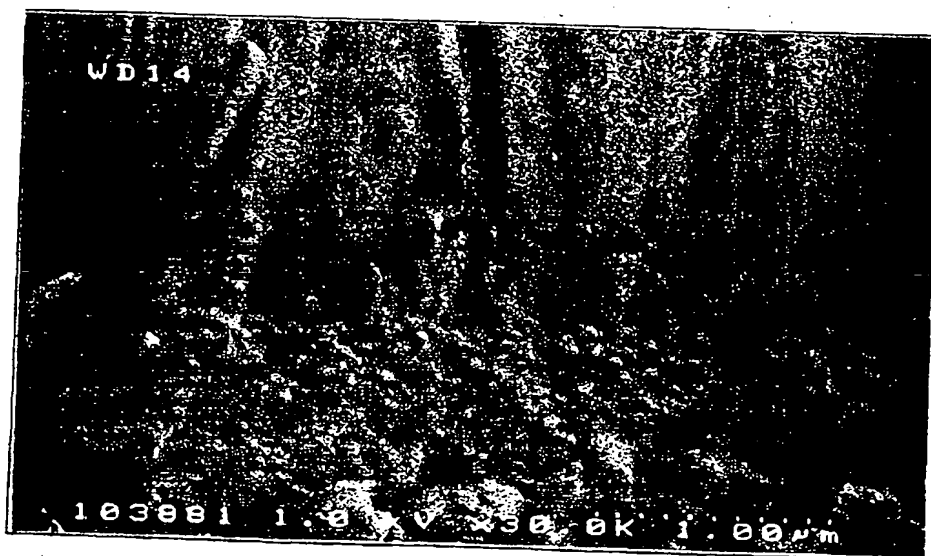
Fig.6. (A)



—
ZEOLITE
LAYERS

—
SUBSTRATE

Fig.6. (B)



—
ZSM-5
LAYER

—
SILICALITE LAYER

—
NUCLEATION
LAYER

+ SUBSTRATE

Fig.7. (A)



Fig.7. (B)



Fig.8. (A)



Fig.8. (B)



Fig.9. (A)



ZSM-5 LAYER , 180 °C/3Hrs

SILICALITE LAYER , 180 °C/2Hrs

NUCLEATION LAYER
+ SUBSTRATE

Fig.9. (B) ↓



Magnified image of silicalite layer,
indicating defect within this layer.

Fig.10.



ZSM-5 LAYER,
180°C/3Hrs.

SILICALITE LAYER, 180°C/2Hrs.

NUCLEATION LAYER
+ SUBSTRATE

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Fig.11.

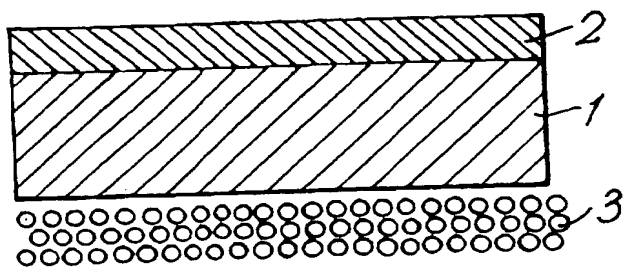


Fig.12.

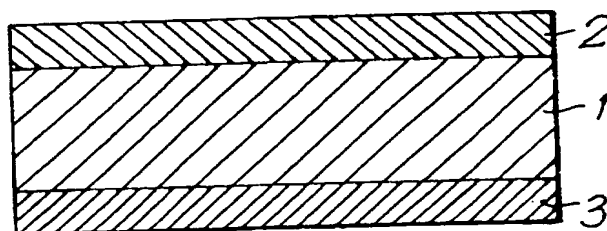


Fig.13.

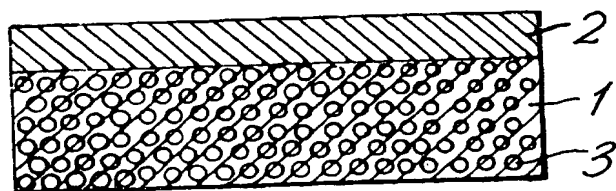


Fig.14.

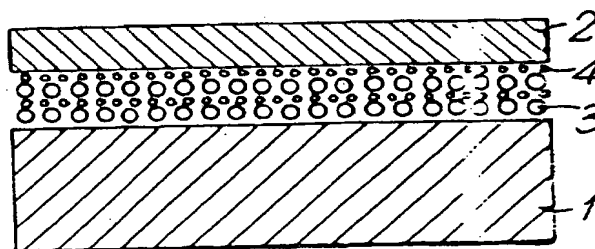


Fig.16.

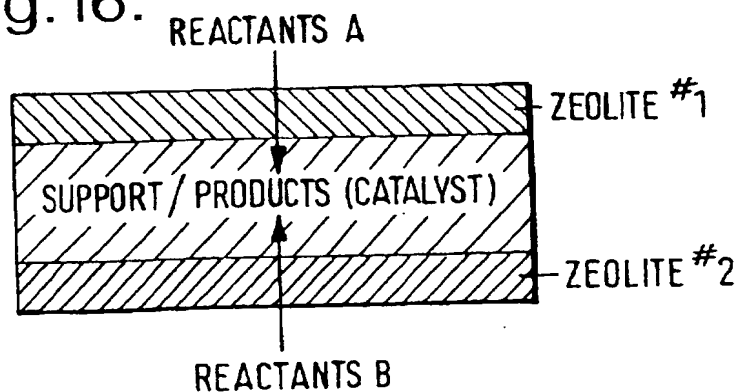
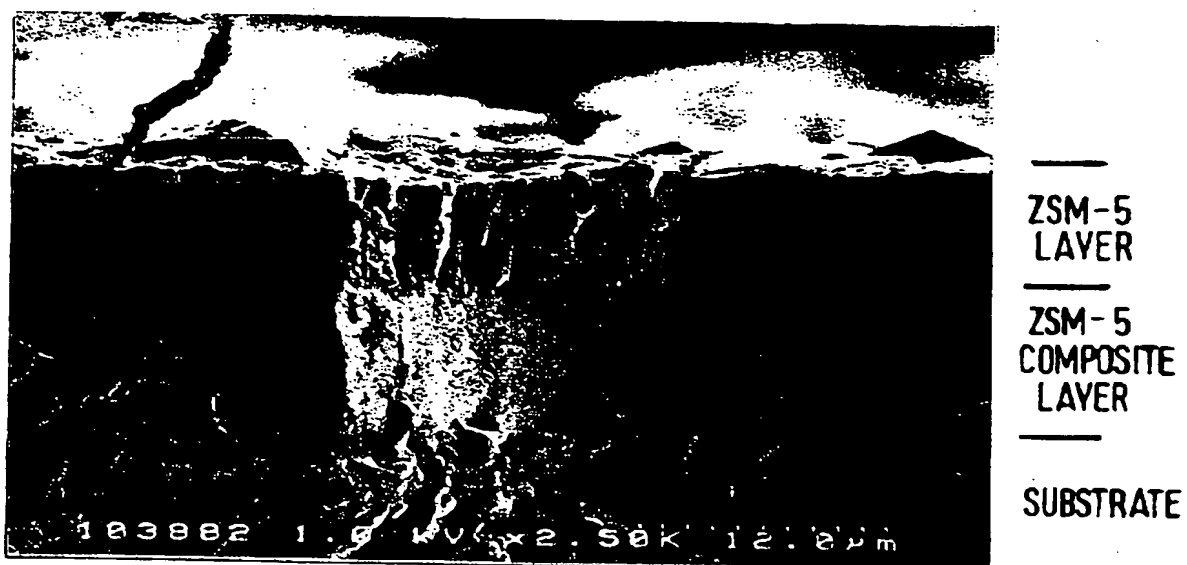


Fig.15.



MOLECULAR SIEVE COMPOSITIONS

FIELD OF THE INVENTION

The present invention is directed towards molecular sieve compositions having two or more independently selected molecular sieve layers, at least one of which is permselective. The invention includes catalytic molecular sieve compositions and catalytic or non-catalytic molecular sieve compositions used in combination with non-molecular sieve catalytic materials.

BACKGROUND OF THE INVENTION

Molecular sieve membranes such as zeolite membranes have been proposed for uses such as molecular separations, reactions, and combined separations and reactions. Such membranes, sometimes referred to as molecular sieve membrane composites or zeolite membrane composites, comprise a zeolite layer, or other inorganic layer capable of molecular separations, on porous or solid substrates. The membranes may also include optional growth enhancing layers, seed layers, and reparation layers. Additionally, the zeolite layer may be used in conjunction with catalytic activity in the form of a proximately located catalytically active material or such catalytic activity may be present in the layer itself, in some cases inherently or for example by ion exchange.

However, some separation, reaction, or combined separation/reaction processes cannot be performed with zeolite membranes known in the art. Some examples of such processes include cases where the catalytic functionality is in the form of catalyst distributed, sometimes with a binder, on or in one or more layers of the membrane. Unfortunately, such membranes would be subject to catalyst attrition. Binder contamination is also a problem, especially in cases where the binder is itself catalytic. There is a need therefore for new combinations of zeolite membranes with catalytic functionality and new means for their manufacture.

It is further desirable to be able to provide compositions, which may be utilised, for staged separation. In staged separations, one or more reactants are separated from a reactant source by a zeolite or zeolite-like layer. One or more additional layers may be used to further separate the reactants, reactants and products, or products formed in or between the layers. A further desirable option would be to combine staged separation with catalytic activity in order to provide combined staged separation with catalytic reaction or staged catalytic reaction. Monolithic structures containing two or more zeolite layers in combination with catalytic functionality and capable of staged separation are not known in the art. Obstacles to forming such compositions include materials-based incompatibilities between the individual layers and between layers and particulate or layer-based catalytic functionality, and difficulties associated with the methods of manufacturing multiple layers of zeolite.

Therefore, there also remains a need for zeolite membrane compositions having two or more zeolite layers and capable of separations, reactions, and combined reaction and separation wherein the catalytic functionality is either an integral part of the membrane or chemically bound to the membrane, especially when the catalytic functionality is in the form of a membrane. In particular, there is a need for a monolithic composition capable of separation, reaction, and combined reaction and separation having at least two zeolite layers in contact, the layers being composed of independently selected zeolite.

SUMMARY OF THE INVENTION

In a first aspect, the invention provides a molecular sieve composition comprising:

- a) a permselective layer of dense, columnar, polycrystalline molecular sieve material,
and

- b) a second independently selected layer of polycrystalline molecular sieve material, the second layer having a surface in contact with a surface of the permselective layer.

In a second aspect, the invention provides a molecular sieve membrane composite composition comprising:

- a) a permselective layer of dense, columnar, polycrystalline molecular sieve material deposited on a substrate, and
- b) a catalytically active region which is not in direct contact with the permselective layer.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows an example of the first aspect wherein the second layer (3) has catalytic functionality and is in contact with a molecular sieve membrane separation layer (2) that is in contact with a support (1).

Figure 2 shows an example of the first aspect wherein the second layer (3) has catalytic functionality and is in the form of a molecular sieve layer which has intergrown with a molecular sieve membrane separation layer (2), the separation layer being in contact with a support (1).

Figure 3 shows an example of the first aspect wherein the second layer (3) is a catalytic functionality which has been incorporated into a region of the molecular sieve membrane separation layer (2) during synthesis of layer (2) which is in contact with a support (1).

Figure 4 shows an example of the first aspect in which a molecular sieve membrane comprising two permselective molecular sieve layers (#1 and #2) ; this being suitable for a staged separation process is illustrated.

Figure 5 shows an example of the first aspect in which staged separation is combined with reaction.

Figures 6, 7, and 8 are electron micrographs showing cross-sections of Examples 7, 9, and 11, respectively, from Table 1. Two magnifications are shown for each.

Figure 9 shows an example of the first aspect where a ZSM-5 layer has been grown on a calcined silicalite layer. Two magnifications are shown.

Figure 10 shows an example of the first aspect where a ZSM-5 layer has been grown on a silicalite layer where the silicalite layer has not been calcined.

Figure 11 shows an example of the second aspect wherein a molecular sieve layer (2) on a porous support (1) has catalyst particles (3) deposited loosely thereon.

Figure 12 shows an example of the second aspect wherein a porous support (1) is situated between a permselective molecular sieve layer (2) and a catalyst layer (3).

Figure 13 shows an example of the second aspect wherein a supported permselective molecular sieve layer (2), which is located on a support (1) which has catalytic functionality (3) contained therein.

Figure 14 shows an example of the first aspect wherein a permselective molecular sieve layer (2) is in intimate contact with a seed layer (4) which contains catalytic functionality (3) which in turn is in contact with a porous support (1).

Figure 15 is an electron micrograph the composite illustrated schematically in figure 14.

Figure 16 schematically represents an example of the second aspect in which a composition of a molecular sieve layer on a porous support that is in contact with a second molecular sieve layer. The support has an internal catalytic functionality. The figure also schematically illustrates the use of such a composition in a reaction involving both reaction and separation.

DETAILED DESCRIPTION OF THE INVENTION

In a first aspect the invention is a monolithic molecular sieve membrane composite capable of separation, reaction, and combined reaction and separation comprising at least two independently selected molecular sieve layers in contact with each other. In a second aspect the invention is a monolithic molecular sieve membrane composite comprising at least one permselective molecular sieve layer and a second layer, which may also be permselective molecular sieve layer, and the layers having a support situated there between. Process applications in which the invention can be used include separations of molecular species, catalytic reactions and reactions which combine reaction and separation. The composition may contain a porous substrate in contact with one of the molecular sieve layers or a permeable intermediate layer situated between the support and one of the molecular sieve layers. Intermediate layers may also be situated between the molecular sieve layers. The invention is compatible with reparation and selectivity-enhancing coatings on the molecular sieve layers. It is to be understood that in relation to the first aspect of the present invention that the two layers are considered to be in contact with each other even if there is present a molecular sieve seeding layer between them which has been utilised in the deposition process for the second layer.

Preferably when the first aspect is utilised for staged separation the second layer is a permselective layer of dense, columnar, polycrystalline molecular sieve material.

Preferably for combined reaction and separation the composition of the first aspect has a second layer which is not dense but has been manufactured utilising the seeded hydrothermal synthesis method described below.

Preferably layer one of the first aspect is a silicalite-1 permselective membrane and the second layer comprises a zeolite catalyst, preferably ZSM-5.

With reference to the second aspect preferably the first layer is a silicalite-1 permselective membrane and the catalyst region is zeolitic preferably ZSM-5.

Advantageously, the molecular sieve layers included in the compositions of the invention are formed from crystals that are contiguous, i.e., substantially every crystal is in contact with one or more of its neighbors. Such contact may be such that neighboring crystals are intergrown, provided they retain their identity as individual crystals. In a preferred embodiment, the crystals in the layer are closely packed.

It is preferred that the permselective layers crystals are such that nonselective permeation paths through the layer are blocked by the narrowest point of approach between crystals. Non-selective permeation pathways are taken to be permeation pathways, which exist at room temperature that do not pass through the molecular sieve crystals. This blockage of nonselective permeation pathways can exist at room temperature after a template, which occludes the pore structure is removed from the molecular sieve crystals. Templates used to aid in the crystallization of molecular sieves may be removed by a calcination step; intergrown molecular sieve crystals (within a layer) should exhibit a blockage of nonselective permeation pathways after the template is removed. A preferred permselective dense molecular sieve layer is formed such that there exists at least one point on a crystal that is less than 20 Å from a point on an adjacent crystal. Between these points can be inorganic oxide material that restricts nonselective permeation of molecules through the layer. The spacing between

molecular sieve crystals in this dense intergrown molecular sieve layer can be established by TEM or with dye permeation tests.

Preferably in one embodiment of the first aspect the substrate is in contact with a mesoporous, crystalline or polycrystalline intermediate layer of a catalytic functionality ranging in size from about 0.1 to about 100 micrometers and nanocrystalline or colloidal-sized zeolite, the intermediate layer being in contact with a dense layer of columnar zeolite crystals having pore openings wherein 99% of the columnar zeolite crystals have at least one point between adjacent crystals that is less than or equal to 20 Å.

The absence of nonselective permeation paths can be detected by methods known in the art and set forth in U.S. Patent No. 5,716,527, and U.S. Patent No. 5,763,347 incorporated by reference herein.

Monolithic compositions of the present invention may include a support material in contact with one or more of the molecular sieve layers. The support may be porous or non-porous. As examples of porous supports, there may be mentioned porous glass, sintered porous metals, e.g., steel such as stainless steel or nickel, an inorganic oxide, e.g., alpha-alumina, titania, cordierite, zeolite as herein defined or zirconia and mixtures of any of these materials. In this context porous supports include supports which have pores which are occluded; such supports whilst having pores are not generally suitable for membrane separation applications but may be used for catalytic applications or separation processes which are not membrane separation processes.

The pore size and porosity of the support should be compatible with the process employed for manufacturing the molecular sieve layer or layers. The support may be any material compatible with the coating and synthesis techniques utilised in the process of the present invention. For example porous alpha-alumina with a surface pore size within the range of 0.08 to 1 µm, most preferably from 0.08 to 0.16 µm, and advantageously with a narrow pore size distribution. Ideally the support should have a relatively high degree of porosity so that the support has an insignificant effect on flux

through the finished product. Preferably the porosity of the support is 30% by volume or greater. The support may be multilayered; for example, to improve the mass transfer characteristics of the support, only the surface region of the support in contact with the molecular sieve or a catalytic layers may have small diameter pores, while the bulk of the support, toward the surface remote from the deposited layer or layers, may have large diameter pores. An example of such a multilayered support is an alpha-alumina disk having pores of about 1 μm diameter coated with a layer of alpha-alumina with pore size about 0.1 μm . A further example of a multilayered support is a large pore metal based support which has an inorganic layer deposited thereon of smaller pore size compared to the metal support. Suitable supports include the composite membranes and layers manufactured according to US 4 981 590 and US 5 089 299.

The molecular sieve layers of the invention may be hydrothermally formed by contacting the substrate or preformed molecular sieve layers if present, or if present the seed layer with a molecular sieve synthesis mixture, and heating for a time and at the temperature sufficient to effect crystallization. Contacting as used herein includes total and partial immersion. When a seed layer is used, the contacting of the substrate or molecular sieve layer with the seed layer, ideally and preferably is carried out such that there is no settling of crystals formed in the synthesis mixture during hydrothermal treatment onto the seed layer.

The permselective molecular sieve layers may be manufactured using hydrothermal synthesis techniques, which are well known in the art. For example suitable methods of manufacture of molecular sieve layers are described in US 5 110 478, US 5 100 596, US 5 019 263, US 5 069 794, EP 0 481 658, EP, 0 481 659, EP 0 481 660, EP 0 632 743, NL9100217, NL9101126, NL9101148, NL 9201204 and WO 94/25151. The disclosures of which in so far as they relate to deposition of molecular sieve layers are incorporated by reference.

The preferred method for the manufacture of the permselective molecular sieve layer or layers is the seeded or nucleated hydrothermal synthesis methods. These

methods are described in WO 96/01683, WO 96/01685, WO 96/01686, WO 96/01687 and PCT/EP97/01267, the disclosures of which is incorporated by reference. In addition other layers of the compositions of the present invention may also be manufactured using this technique even if they are not permselective.

In this method the seed layer comprises molecular sieve crystals of average particle size 200 nm or less. Advantageously, the crystal size of the molecular sieve in the seed layer is 100 nm or less ideally within the range 5 to 100 nm and most preferably within the range 25 to 75 nm.

The seed layer advantageously consists essentially of the molecular sieve material, or may be a composite of the molecular sieve material and intercalating material. The particles of the seed layer may be contiguous or non-contiguous; preferably they are contiguous. The intercalating material may be the same material as the support.

The colloidal molecular sieve seed crystals may be prepared by processes which are well known in the art, such as those described in International Applications WO93/08125, WO97/03019 WO97/03020 WO97/03021 and WO94/05597, the disclosures of which in so far as they refer to the manufacture of colloidal seeds and there use in the manufacture of layers, are incorporated by reference.

The seed layer may be applied to the support or deposited molecular sieve layer or layers by techniques known in the art, for example, spin-coating, wash-coating, spray-coating, brushing, slip-casting or dip-coating in a suspension of the colloidal molecular sieve crystals. The colloidal crystals are preferably applied by spin-coating, the viscosity of the mixture and the spin rate controlling the coating thickness.

The thickness of the seed layer is preferably 2 μm or less, most preferably at most 1 μm or 0.5 μm or less. Advantageously, the seed layer is of sufficient thickness to cover irregularities of comparable scale in the surface of the support or molecular

sieve layer onto which it is deposited. Advantageously, the seed layer is at most the thickness of the subsequently deposited molecular sieve layer.

In one embodiment the seed layer may be deposited and used as a monolayer. Such a monolayer and its method of deposition is described in WO97/33684, the disclosure of which in so far as it relates to the manufacture of a seed monolayer is incorporated by reference.

In one embodiment of the process of the present invention the support or molecular sieve coated support may be placed into the molecular sieve synthesis mixture without any further treatment of the seed layer after its deposition thereon. Even when submerged in the synthesis mixture, the particles in the seed layer remain adhered to the support and facilitate growth of the molecular sieve layer. However, under some circumstances, e.g. during stirring or agitation of the synthesis mixture, the adhesion between the particles and the support may be insufficient and steps must be taken to stabilise the seed layer.

Therefore, in a further embodiment of the invention, the seed layer is stabilised before being placed into the synthesis mixture. This stabilisation can be achieved in one aspect by heat-treating the seed layer, e.g. at temperatures between 30 and 1000°C, ideally greater than 50°C and more preferably between 200°C and 1000°C and most preferably greater than 300°C and between 400°C and 600°C for several hours preferably at least two hours most preferably 2 to 10 hours.

In a further embodiment the seed layer molecular sieve crystals are synthesized in situ on the support or molecular sieve layer or layers before the hydrothermal deposition of a subsequent molecular sieve layer. According to this embodiment, the process comprises preparing a first synthesis mixture comprising a source of silica and an organic structure directing agent in a proportion sufficient to effect substantially complete dissolution of the silica source in the mixture at the boiling temperature of the mixture, contacting the support in the synthesis mixture, crystallizing molecular sieve from the synthesis mixture onto the support or layers, to form the seed layer. This

procedure may be carried out as described in the above-mentioned Application WO 94/25151. The resulting coated support or layer is then immersed in a second synthesis mixture and subjected to hydrothermal treatment to produce a molecular sieve layer according to the present invention.

The composition of the synthesis solution is selected to provide the desired molecular sieve layer and such appropriate synthesis solution compositions are provided in the above identified prior art references. When the molecular sieve layer comprises silica in its framework then the H_2O to SiO_2 ratio ideally is within the range of 7 to 60. In a preferred embodiment the silicon source comprises colloidal silica. Preferably the H_2O to SiO_2 ratio is within the range of 7 to 30 and most preferably within the range 7 to 20. For certain molecular sieves such as aluminophosphates a source of silica is not required.

The composition of the synthesis mixture varies according to the process; the mixture always contains sources of the various components of the desired molecular sieves and usually contains a structure-directing agent. A preferred colloidal silica source is an ammonia-stabilised colloidal silica, e.g., that available from du Pont under the trade mark Ludox AS-40. The source of silicon may also be the source of potassium, in the form of potassium silicate. Such a silicate is conveniently in the form of an aqueous solution such, for example, as sold by Aremco Products, Inc. under the trade mark CERAMA-BIND, which is available as a solution of pH 11.3, specific gravity 1.26, and viscosity 40 mPas. Other sources of silicon include, for example, silicic acid. As other sources of potassium, when present, there may be mentioned the hydroxide. Whether or not the synthesis mixture contains a potassium source, it may also contain sodium hydroxide to give the desired alkalinity.

The structure directing agent, when present, may be any of those commonly used in molecular sieve synthesis. For the manufacture of an MFI layer, a tetrapropylammonium hydroxide or halide is advantageously used. For the manufacture of an MFI type zeolite, especially ZSM-5 or silicalite-I, the synthesis mixture is

advantageously of a molar composition, calculated in terms of oxides, within the ranges:

$M_2O:SiO_2$	0 to 0.7 to :1 preferably 0.016 to 0.350:1
$SiO_2:Al_2O_3$	12 to infinity :1
$(TPA)_2O:SiO_2$	0 to 0.2:1 preferably 0 to 0.075 :1
$H_2O:SiO_2$	7 to 60:1 preferably 9 to 30 :1

wherein TPA represents tetrapropylammonium and M an alkali metal, preferably sodium or potassium, but also Li, Cs and also ammonia. Other template agents may be used in these ratios.

A preferred route for MFI zeolites, e.g., is from a Low Alkaline synthesis mixture having a pH of about 6 to about 13 preferably about 8 to about 13, and from which MFI zeolite crystals can be grown. Such mixtures are readily prepared by those skilled in the art. For example, suitable mixtures include Na_2O , TPABr ("tetrapropylammoniumbromide), SiO_2 and water. The synthesis mixture is then heated to about 50 to about 300°C, preferably about 180°C, for a period of about 30 minutes to about 300 hours, preferably for about 30 minutes. After crystallization, the supported layer may be washed in hot water for a time sufficient to remove un-reacted synthesis material, dried, and calcined by methods known in the art.

In this specification ratios with infinity as the value indicate that one of the ratio materials is not present in the mixture.

Heating times generally may be, for example, in the range of from 30 mins to 12 days, preferably from 30 mins to 4 days most preferably less than 100 hours ideally 30 mins to 80 hours. Temperatures may be, for example, from 50 to 300°C, preferably from 90 to 200°C most preferably 180°C or less.

In a preferred aspect the process of the present invention utilises a hydrothermal synthesis temperature of 140°C or less, preferably within the range from 60 to 100 °C, and most preferably within the range 60 to 90°C.

The hydrothermal treatment advantageously is undertaken in an autoclave under autogenous pressure. However with synthesis temperatures below 100°C it is possible to undertake the synthesis under ambient pressure conditions.

After crystallisation, the structure may be washed, dried, and the molecular sieve calcined. The calcination conditions preferably comprise slow heating and cooling to ensure that the structure, and in particular the molecular sieve layer, remains intact. Preferably the structure is calcined at a temperature of 350 to 600°C, preferably 450 to 550°C.

In relation to the processes described herein contacting is to be understood to include immersion or partial immersion of the substrate in the relevant molecular sieve synthesis mixture.

Mesoporous and microporous intermediate layers may be present in the invention between a molecular sieve layer and a support, between molecular sieve layers, and between molecular sieve layers and catalytic layers. Such intermediate layers are known in the art, and are set forth in the referenced patents.

The molecular sieve layer may be any known molecular sieve material; for example it may be a silicate, an aluminosilicate, an aluminophosphate, a silicoaluminophosphate, a metalloaluminophosphate, or a metalloaluminophosphosilicate. The preferred molecular sieve will depend on the chosen application, e.g. separation, catalytic applications, and combined reaction and separation, and on the size of the molecules being treated. There are many known ways to tailor the properties of the molecular sieves, for example, structure type, chemical composition, ion-exchange, and activation procedures.

Representative examples are molecular sieves/zeolites which may be used in the molecular sieve layer include the structure types AFI, AEL, BEA, CHA, EUO, FAU, FER, KFI, LTA, LTL, MAZ, MOR, MEL, MTW, OFF, TON and, especially, MFI.

The structure types of the seed and molecular sieve layers may be the same or different. Further, if the structure types are the same, the compositions may be the same or different.

Some of the above materials while not being true zeolites are frequently referred to in the literature as such, and this term will be used broadly in this specification.

The molecular sieve layers of the present invention may be treated to further improve or stabilise their properties. In one aspect, whilst intact layer regions are of good quality, there may be regions of the layer which are cracked or where there may be pinholes present. If these cracks and pinholes are of such quantity and dimensions that they have a disproportionate effect on membrane performance then it is useful to reparate the layer. Suitable reparation techniques are described in for example WO96/01682, WO96/01686 and WO97/25129, the disclosures of which are incorporated by reference. The preferred method of reparation is that described in WO96/01686. If the molecular sieve layer of the present invention has no pinholes or cracks which disproportionately effect the layer performance it may still be advantageous to treat the molecular sieve layer to maintain its performance. In this context a suitable treatment is the selectivity enhancing layers described in WO96/01686. Such selectivity enhancing layers may at the same time also reparate defective molecular sieve layers.

The thickness of the molecular sieve layers is within the range 0.1 to 150 μm , preferably from 0.5 to 20 μm . The thickness of each layer is independently selected.

The thickness of the molecular sieve layer is advantageously for some applications less than 2 μm ideally within the range of 0.1 to 2 μm , more advantageously from 0.1 to 1 μm , and preferably from 0.1 to 0.5 μm . Advantageously, the thickness of the layer and the crystallite size of the molecular sieve are such that the layer thickness is approximately the size of the longest edges of the crystals, giving essentially a monolayer. The molecular sieve crystals forming the molecular sieve of the invention are as set forth in the referenced patents, as are the layers' structure, spatial and crystallographic orientation, and defect and void concentration. Such properties may be individually selected in each layer of the invention. Advantageously the crystals of the molecular sieve layer exhibit a columnar Shape Preferred Orientation.

It has been observed that one difficulty associated with the deposition of molecular sieve layers upon already preformed molecular sieve layers is that the already preformed molecular sieve layer results in erosion (or corrosion) of the first layer; this is demonstrated in Figure 9. This can reduce the effectiveness of the first layer. It has surprisingly been found that this may be significantly reduced if the deposition of the second layer is undertaken prior to calcination of the first layer. It is believed that this erosion results from interactions between the calcined layer and the synthesis solution. When a second layer is grown on a molecular sieve layer that has not been calcined, no erosion is observed; see Figure 10. It is believed that the template material such as tetrapropylammonium bromide protects the underlying layer during synthesis of the second layer. Such templates decompose during calcination and would consequently offer no protection to a calcined layer.

Accordingly the present invention in a further aspect provides a process for the manufacture of a molecular sieve composite composition comprising:

- a) a permselective layer of dense, columnar, polycrystalline molecular material, and

- b) a second independently selected layer of polycrystalline molecular sieve material, the second layer having a surface in contact with a surface of the permselective layer;

which process comprises deposition of the second layer prior to calcination of the first layer.

A preferred synthesis technique used with this invention is the growth of molecular sieve crystals on the face of a molecular layer, a support, or intermediate layer which is oriented from 90 to 270 degrees in a synthesis mixture, as set forth in the referenced patents.

The compositions of the invention are selective molecular separators. Such compositions, as set forth herein are useful for all separations, reactions, and combined reactions and separations set forth herein and in the referenced patents.

Depending on the nature of the desired process, i.e. whether it involves reactions, separations, or a combination of separations and reactions, the composition may be in the form of a composite. The composites shown in Figures 1 through 3 and 11 to 14 are illustrative of the invention, and are not meant to be limiting. Combinations of two or more of the composites are within the scope of the invention. The illustrated composites have molecular sieve layers in contact with other molecular sieve layers and supports, but compositions having intermediate layers situated there between as set forth in the referenced patents are also within the scope of the invention. Such intermediate layers are also set forth in PCT publication WO 96/01687, incorporated by reference herein. The illustrated composites are shown for simplicity in planar form, i.e. as layers having a small thickness compared to surface area. Concentric tubular composites are also within the scope of the invention, and such composites may be in monolithic or honeycomb form. A molecular sieve layer or substrate may be the innermost, inner, or outermost concentric layer of the tube or monolith.

Figure 1 shows an embodiment where the catalytic functionality is in contact with a molecular sieve separation layer that is in contact with a support. This embodiment is useful in processes in which it is desirable for separation and catalysis to occur on the same side of the support.

Figure 2 shows an embodiment wherein the catalytic functionality is in the form of a molecular sieve layer intergrown with a molecular sieve separation layer, the separation layer being in contact with a support. The catalyst layer may be epitaxial with the separation layer. Both molecular sieve layers may be formed in accordance with the synthesis methods set forth herein, although it may be desirable for the catalytic layer to have a large number of grain boundaries and defects in order to increase catalyst surface area. In a related embodiment, the catalyst layer is slip coated or cast according to methods known in the art and then affixed to the separation layer. In another related embodiment, the catalytic functionality is incorporated into a region of the separation layer, as set forth in Figure 3. Advantageously, the composition may be formed in a single growth reaction with the addition of the catalytic functionality or its precursor occurring near the end of the synthesis in order to incorporate the catalytic functionality into the outermost zone of the separation layer. This growth may take the form of secondary growth (i.e. multiple *in situ* hydrothermal syntheses, with or without seeding), post-synthetic treatment (e.g. treatment with an Al-O source to incorporate acidic Al-O-H into the system), or introduction of an alumina source into the primary reaction mixture after a specific period of time resulting in a molecular sieve layer with a varying Si/Al composition in different zones. The embodiment of Figure 3 is advantageous in processes where close proximity is desirable between the catalytic and separation functionalities and where it is desirable for the catalytic layer to reparate the separation layer.

Thus in a further aspect the present invention provides for a process for the manufacture of a composite according to the first aspect in which process catalytic

functionality or a precursor thereof is added to the synthesis process for the deposition of the first layer after commencement of the synthesis, and the resultant catalytic region constitutes the second molecular sieve layer.

Preferably the catalytic functionality or precursor is added after at least 50% of the first layer has been deposited on the support.

In the second aspect of the present invention the catalytically active region may be formed from a slurry containing molecular sieve according to methods known in the art.

The molecular sieve composites shown in Figures 11, 12 and 13 are illustrative of the second aspect of the present invention and are not meant to be limiting.

In the composition illustrated in Figure 11, a permselective molecular sieve layer is in contact with one side of a porous support. The other side of the support is in contact with a catalytic functionality such as loosely bonded catalyst particles. The embodiment of Figure 11 is especially useful in processes requiring periodic catalyst replacement and in processes requiring post-synthesis molecular sieve layer reparation. Catalyst-membrane abrasion is also avoided in this embodiment. Preferably the catalyst comprises molecular sieve especially a zeolite catalyst.

In another embodiment illustrated in Figure 12, a porous support is situated between a catalyst layer and a molecular sieve separation layer. The layers may be formed according to the methods set forth herein; the catalyst layers may, alternatively, be formed by slip-coating or casting methods known in the art. Preferably the catalyst is deposited by hydrothermal synthesis.

A catalytic functionality may also be present in the support (Figure 13). Advantages related to including the catalytic functionality in the support material include ease of fabrication and relatively low mass transfer resistance.

In a further embodiment of the first aspect of the present invention the catalytic functionality may be present in a seed layer situated between the support and the separation layer (Figures 14 and 15).

When the catalytic functionality is located in the intermediate layer, the layer may be in the form of catalytically active seeds or a composite of seeds and catalyst such as a layer of seeds deposited on a layer of catalyst. Such seed layers and their formation are set forth in the referenced patents. Sub-micron-sized and larger catalyst particles that may be molecular sieves may be incorporated into the nucleation layer with or without a binder. Surprisingly, the presence of such particles does not diminish the seed layer's effectiveness in nucleating an intergrown molecular sieve membrane. An electron micrograph shown in Figure 15 shows a porous substrate having a seed layer containing ZSM-5 particles of about 1 micron diameter, with an intergrown ZSM-5 layer thereon. The catalyst particles may range in size from about 0.1 to about 100 micrometers, preferably from about 1 to about 100 micrometers, and more preferably from about 10 to about 100 micrometers.

Molecular sieve compositions of the invention may be utilized to conduct a wide variety of separations based on their molecular sieving capabilities. Their performance is largely determined by their framework geometry (pore structure) and framework composition. Additionally, their separations behavior may be influenced by extra-framework, charge-balancing cations, which may reduce access to, or mobility through their internal pore network. Thus, diffusivity of a molecular species through a molecular sieve pore system (for components which are not restricted from entering the pore because of a prohibitively large kinetic diameter) may be restricted by cations

residing within the channel and influenced by interactions with the atoms encountered at the channel surface.

It may be desirable to separate a mixture of components utilizing these two phenomena (size exclusion (pore restriction) and surface interaction) in various combinations. For the case of two distinct molecular sieve layers on a membrane support, see Figure 4, there exist four possible architectures: (i) where molecular sieves 1 and 2 are both separating molecules based on size; (ii) where molecular sieves 1 and 2 are both separating based on interactions of molecules at their pore surfaces; or (iii and iv) where each separation phenomenon singly dominates in one of the two molecular sieve layers.

Processes involving acid- and/or metal-catalyzed reactions are within the scope of the invention. The properties exhibited by a specific material may depend on (i) the framework structure and composition of the molecular sieve; (ii) both the framework and non-framework (i.e. detrital) atoms of the material; (iii) inherent or exchanged cations; (iv) metals impregnated into the material (typically post-synthesis); (v) any other post-synthetic treatment such as selectivation, coking, or silanation.

In one such process shown in Figure 16, two reactant mixtures are separated and run through two different molecular sieve catalyst layers, with the option for reaction at a third catalytic site within the layer support. Benefits accruing from the use of the invention's compositions in such processes include selectivity enhancement of a catalytic reaction, strict control of reaction stoichiometry, reaction rate enhancement, limiting which reactants 'see' the catalyst, and protection of a catalyst from deactivation by contaminants in the reaction mixture. Multiple layers can also be used on either side of a support to separate components from two different reaction mixtures so that a limited number reactants react at catalytic sites within a support.

It may be desirable to conduct two reactions simultaneously, or successively, in a single system utilizing a single reaction mixture, or two different, separated mixtures.

In the first case, simultaneous or successive reactions (for example, acid-catalyzed, metal-catalyzed, or both) could be affected by the use of multiple layers of supported molecular sieve catalysts as in Figure 5.

As set forth herein, multiple layers of molecular sieves can also be utilized to combine reaction and separation within a single system. Benefits accruing from the use of the invention's compositions in such processes include selectivity enhancement of a catalytic reaction, strict control of reaction stoichiometry, reaction rate enhancement, limiting which reactants 'see' the catalyst, and protection of a catalyst from deactivation by contaminants in the reaction mixture. Multiple layers can also be used on either side of a support to separate components from two different reaction mixtures so that a limited number reactants react at catalytic sites within a support.

A particularly advantageous use of the compositions of the invention involves producing species in concentrations above equilibrium in equilibrium-limited catalytic reactions, especially in equilibrium limited isomerization reactions of xylenes isomers. The use of the compositions of the present invention in such a process is set forth in more detail below.

Maintaining a constant feed of equilibrium xylene isomers is critical to the success of a molecular sieve membrane separation system for enhancing production of para-xylene because the feed is quickly depleted of para-xylene by the membrane. In the practice of this invention, this is accomplished by combining an isomerization catalyst with the permselective membrane transport system.

Such an isomerization catalyst may be one of the known aromatic isomerization catalysts, including acidic materials such as ZSM-5 and precious metal catalysts. The catalytic functionality should be properly positioned within the reactor membrane system relative to the separation layer. It is advantageous to keep the catalyst in very close proximity to the separation functionality of the membrane system so that a constant source of para-xylene is available to the membrane (i.e. the catalyst quickly re-

equilibrates the remaining xylene isomers to maintain a source of para-xylene). Separating the two components by a significant distance may require back diffusion by the para-depleted feed to re-establish equilibrium, thus lowering the overall efficiency of the system.

Several other criteria, in addition to catalyst placement and selection, have a bearing on combining the catalytic and separation functionalities. The effective reactivity of the catalytic component should be sufficient to constantly maintain isomer equilibrium; i.e. catalytic reactivity must be greater than the rate of para-xylene removal. The reactivity is controlled by several factors including (using an acid catalyst such as ZSM-5 as an example): (i) process conditions; (ii) framework silica/alumina ratio, which generally determines the acidity, and therefore, the activity of the catalyst; and (iii) the amount of catalyst, or more specifically, catalyst surface area, available for reaction.

The framework composition of the acidic molecular sieve is largely determined by the hydrothermal reaction conditions established for the crystallization of the material as set forth herein and in the referenced patents. In the absence of any alumina source, the MFI structure resulting from a tetrapropylammonium cation-directed synthesis is completely devoid of any framework aluminum (silicalite-1) and, consequently, any catalytic activity. This structure is ideal, however, for separation of para-xylene from its isomers because it is incapable of converting para-xylene back into an equilibrium mixture (its pore size is also suitable for this molecular separation). However, the presence of alumina and, depending on hydrothermal reaction conditions, aluminum incorporation into the framework, provides a source of Brönsted acidity necessary for catalytic isomerization.

Catalyst volume, surface area, regeneration, and replacement considerations also have a bearing on the use of the compositions of the invention in para-xylene production. For loose catalyst particles, a volume of sufficient size to contain the amount of catalyst required (to maintain xylenes equilibrium for the membrane) is necessary. Care must be taken when positioning loose particles in direct contact with

the thin molecular sieve separation layer in order to avoid abrasion. Regarding catalyst regeneration and replacement, important criteria include the choice of feed/sweep flow (counter- vs. co-current), hydrogen requirements, heat effects, and the need for cross-cut channels to improve overall system flow.

Regardless of whether an integrated catalyst architecture or a loose catalyst is chosen, the catalytic functionality should be present in a sufficient amount to establish thermodynamic equilibrium and should minimally limit the overall mass transfer of the system. Consequently, continuous defect-free ZSM-5 overlayers are not desirable as catalytic regions because of the xylene transport limits in this material.

The invention is further illustrated in the following non-limiting examples.

EXAMPLES

In these examples the silicalite-1 permselective layers were prepared using the general seeding hydrothermal method referenced above.

The supports utilised were:

- A) Alpha alumina of 0.1 μm pore diameter
- B) alpha alumina of 1 μm pore diameter.
- C) An asymmetric support of theta alumina deposited upon alpha alumina of 0.1 μm pore diameter which was in turn deposited upon alpha alumina of 1 μm pore diameter.
- D) Porous stainless steel.

Colloidal silicalite and colloidal ZSM-5 were prepared in accordance with the procedures identified in the referenced patents.

Hydrothermal synthesis processes were performed using mixtures of the following reagents: NaOH, Ludox HS-40™ (Dupont), tetrapropylammonium bromide (98%), $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and distilled water.

Thin silicalite membranes utilising seeded synthesis were prepared in accordance with methods described in the referenced patents, on porous alumina substrates having about a 0.1 micron pore size, a thin nucleation layer (<1 micron), and a silicalite layer (0.5 micron). In addition thick silicalite membranes were prepared using the seeded method and synthesized at 180°C for 6 and 21 hours on seeded theta-alumina porous alumina of about 0.1 and 1.0 pore size (support (C)). Both thick and thin membranes were washed in hot water for a time sufficient to remove any un-reacted synthesis material.

Example 1. Preparation of Epitaxial ZSM-5 on a Silicalite Membrane

In a hydrothermal reaction, the ZSM-5 layer was prepared from reaction mixtures of NaOH, TPABr, colloidal silica, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and water. The chemical composition of the synthesis solution was 5 Na₂O:100 SiO₂:8000 H₂O: 2 Al₂O₃: 10 TPABr. The 6.4 g of TPABr, 0.94 g of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and 2.05 g of NaOH (50 wt.%) were dissolved in 300 ml of distilled water with stirring. To this solution, 37.6 g of Ludox HS-40 was then added with agitation for at least 15 minutes until a uniform solution was formed.

Thick supported silicalite membranes as set forth above were placed in the upper position of a Teflon liner and supported with the stainless steel wire mesh in an inverted orientation. The synthesis solution was then poured into reactor to cover the entire carriers. The autoclave was sealed and placed in an oven, which was preheated to the desired temperature. The reaction time can vary from one hour to several weeks depending on the desired thickness. The reaction bombs were removed from the oven after reaction and cooled to room temperature. The coated membranes were washed with hot water for at least 6 hours, then calcined at 500 °C for 6 hours in air. The

heating rate was controlled at 10 C/hour. The resulting membranes were ion exchanged with 0.1N NH_4NO_3 solution at 80 C for 2 hours, washed with water, dried at 120 C, then calcined at 500 C for 6 hours.

Example 2. Preparation of Seeded ZSM-5 on a Silicalite Membrane

(a) ZSM-5 nucleation layer coating:

The colloidal ZSM-5 was first diluted with distilled water to the concentration of 0.5 wt %. Silicalite membranes as set forth in example 1 were coated with this solution and calcined at 400 C for 6 hours. The heating rate was controlled at 20 C/hr.

(b) ZSM-5 hydrothermal reaction:

A ZSM-5 layer was formed by an in situ crystallization via a hydrothermal reaction. In the reaction, the ZSM-5 layers were prepared from reaction mixtures of NaOH, TPABr, colloidal silica, Al_2O_3 , and water. The chemical composition of the synthesis solution was 5 Na_2O :100 SiO_2 :8000 H_2O : 2 Al_2O_3 : 10 TPABr. The 6.4 g of TPABr, 0.94 g of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and 2.05 g of NaOH (50 wt.%) were dissolved in 300 ml of distilled water with stirring. To this solution, 37.6 g of Ludox HS-40 was then added with agitation for at least 15 minutes until a uniform solution was formed.

Supported silicalite membranes as set forth in example 1 and coated with the nucleation coating as described above were placed in the upper position of a Teflon liner and supported with the stainless steel wire mesh. The synthesis solution was then poured into reactor to cover the entire carriers. The autoclave was sealed and placed in an oven, which was preheated to the desired temperature. The reaction time can vary from one hour to several weeks depending on the desired thickness. The reaction bombs were removed from the oven after reaction and cooled to room temperature. The coated carriers were washed with hot water for at least 6 hours, then calcined at 500 °C for 6 hours in air. The heating rate was controlled at 15 C/hour. The resulting

membranes were ion exchanged with 0.1N NH_4NO_3 solution at 80 C for 2 hours, washed with water, dried at 120 C, then calcined at 500 C for 6 hours.

Example 3. Preparation of MFI Layer on a ZSM-5 Composite Membrane

(a) ZSM-5/Colloidal alumina layer coating:

A coating slurry was prepared from the mixture of ZSM-5 fine powder with Si/Al=24.6 by weight, colloidal alumina(Al-20 from PQ), organic binder (methylcellulose), surfactant, and distilled water. The weight % of ZSM-5:alumina is controlled to 60:40 in this example. Application of the slurry to the substrate can be done by any convenient technique such as spinning, dipping, spraying, or casting, depending on size and geometry of the substrate. Here, a porous alumina substrate having about a 1 micron pore size was coated with the prepared slurry by spin coating, dried at 120 C, and calcined at 500 C for 6 hours. The heating rate was controlled at 20 C/hr.

(b) ZSM-5 hydrothermal reaction:

A ZSM-5 layer was formed by in situ crystallization via a hydrothermal reaction. In the reaction, the ZSM-5 layer was prepared from a reaction mixtures of NaOH, TPABr, colloidal silica, Al_2O_3 , and water. The chemical composition of the synthesis solution was 5 Na_2O :100 SiO_2 :8000 H_2O : 2 Al_2O_3 : 10 TPABr. The 6.4 g of TPABr, 0.94 g of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and 2.05 g of NaOH (50 wt.%) were dissolved in 300 ml of distilled water with stirring. To this solution, 37.6 g of Ludox HS-40 was then added with agitation for at least 15 minutes until a uniform solution was formed.

The synthesis was undertaken as described in Example 2.

Example 4. Preparation of ZSM-5 Composite Layer on a Silicalite Membrane

a) ZSM-5/Colloidal alumina layer coating:

A coating slurry was prepared from the mixture of ZSM-5 with Si/Al=24.6 by weight fine powder, colloidal alumina (Al-20 from PQ), organic binder (methylcellulose), surfactant, and distilled water. The weight % of ZSM-5:alumina is controlled to 60:40 in this study. Application of the slurry to the substrate can be done by any convenient technique such as spinning, dipping, spraying, or casting, depending on size and geometry of the substrate. Here, a supported silicalite substrate as set forth in Example 1 was coated with the prepared slurry by spin coating, dried at 120 C, and calcined at 500 C for 6 hours. The heating rate was controlled at 20 C/hr.

Example 5. Preparation of Seeded ZSM-5 on thin LAI-ISC silicalite membrane on SS or A porous alumina substrate having about a 1 micron pore sizes

(a) Preparation of thin silicalite membrane on Stainless Steel or porous alumina substrates having about a 1 micron pore sizes

The thin silicalite membranes were synthesized at 180 C for 2 hours on a porous stainless steel or alumina support. The synthesis was conducted according to LAI-ISC synthesis methods as set forth in the referenced patents.

(b) ZSM-5 nucleation layer coating:

The colloidal ZSM-5 was first diluted with distilled water to the concentration of 0.5 wt %. The silicalite membranes were coated with this solution and calcined at 400 C for 6 hours. The heating rate was controlled at 20 C/hr.

(c) ZSM-5 hydrothermal reaction:

The next step in the fabrication sequence is forming the ZSM-5 layer through in situ crystallization via hydrothermal reactions. In the reaction, the ZSM-5 layers were prepared from reaction mixtures of NaOH, TPABr, colloidal silica, Al₂O₃, and water. The chemical composition of the synthesis solution was 5 Na₂O:100 SiO₂:8000 H₂O: 2 Al₂O₃: 10 TPABr. The 6.4 g of TPABr, 0.94 g of Al(NO₃)₃·9H₂O, and 2.05 g of NaOH (50 wt.%) were dissolved in 300 ml of distilled water with stirring. To this solution, 37.6 g of Ludox HS-40 was then added with agitation for at least 15 minutes until a uniform solution was formed. The general hydrothermal synthesis conditions are as described above.

Examples 7 to 19

A series of composites were prepared using the procedure described in Examples 1 to 6. The data for these examples is provided in Table 1.

Table 1						
Example	Substrate	Reaction temp	Reaction time	Thickness	Result	Comments
7	A	180 C	24 hrs	~ 27 μm	Columnar ZSM-5	A
8	A	180 C	48 hrs	-	Columnar ZSM-5	A
9	C	180 C	18 hrs	~ 14 μm	Columnar ZSM-5	B
10	C	180 C	18 hrs	~ 14 μm	Columnar ZSM-5	C
11	A	120 C	24 hrs	~ 1.5 μm	Columnar ZSM-5	D
12	A	120 C	42 hrs	-	Columnar ZSM-5	D
13	A	180 C	8 hrs	-	Columnar ZSM-5	D
14	A	180 C	24 hrs	~ 27 μm	Columnar	D

					ZSM-5	
15		180 C	3.3 hrs	-	Columnar ZSM-5	E
16		180 C	6 hrs	~ 8 μ m	Columnar ZSM-5	E
17		180 C	26 hrs	-	Columnar ZSM-5	E
18	D	180 C	12 hrs	-	Columnar ZSM-5	F
19	B	180 C	12 hrs	-	Columnar ZSM-5	G

A: 0.5 μ m silicalite membrane; B: 10 μ m silicalite membrane; C: 30 μ m silicalite membrane; D: seeded 0.5 μ m silicalite membrane; E: ZSM-5 composite membrane(ZSM-5 : alumina = 60 : 40 (wt.%)); F: seeded thin(< 1 -2 μ m) LAI-ISC membrane on SS; G: seeded thin(< 1 -2 μ m) LAI-ISC membrane on porous alumina having about 1.0 micron pore size. " - " data is not available

Detailed morphology of the resulting membranes were examined by SEM. Figures 6, 7, and 8 show the full cross-sectional morphologies of Examples 7, 9, and 11. From the figures it is clear that ZSM-5 layers consist of a continuous array of densely packed and intergrown crystals. The formation of a columnar structure in the molecular sieve layer is apparent. The width of the columns right on the silicalite layer is very narrow and becomes larger and larger as the layer grows. As such, the average grain size of molecular sieve crystals increases with increasing film thickness.

From Figures 6 and 8, it can be seen that there is no morphology difference between the two membrane composites, it is believed that crystallization rate is about the same for samples with seeding or without seeding, 1 micron per hour at 180 C. The micrographs demonstrate that silicalite crystals on a silicalite layer can induce nucleation for ZSM-5 film formation. In other words, a silicalite membrane can be used as a nucleation layer for a regrown process. The evidence of epitaxial ZSM-5 grown on silicalite membrane can be observed more clearly on thick silicalite membrane, such as Example 11. Detailed epitaxial growth morphology from a silicalite membrane was shown in Figure 7.

The $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios of the ZSM-5 films were measured by EDX, and the $\text{SiO}_2/\text{Al}_2\text{O}_3$ is estimated in between 40 to 100.

Example 20

A 0.1 porous alumina substrate was coated with a GEL layer and a 1 micron silicalite layer under hydrothermal conditions at 180°C for 2 hours as set forth in the referenced publication. The sample was washed in hot water for a time sufficient to remove unreacted synthesis material and then calcined at 500°C for 6 hours in air. Thereafter, in accordance with this invention, an epitaxial ZSM-5 layer of about 2 microns thick was hydrothermally grown at 180°C for 3 hours on top of the calcined silicalite layer. See Figure 9. The figure shows that erosion of the silicalite layer occurred during the growth of the ZSM-5 layer. It is believed that the erosion results from synthesis solution etching. Such etching can be ameliorated or substantially prevented by growing the ZSM-5 layer on a silicalite layer that has been washed but not calcined, as shown in Figure 10.

WHAT IS CLAIMED IS:

1. A molecular sieve composition comprising:
 - a) a permselective layer of dense, columnar, polycrystalline molecular sieve material, and
 - b) a second independently selected layer of polycrystalline molecular sieve material, the second layer having a surface in contact with a surface of the permselective layer.
2. A molecular sieve composition as claimed in claim 1 wherein the second layer is a permselective layer of dense, columnar, polycrystalline molecular sieve material.
3. A molecular sieve composition as claimed in claim 1 or claim 2 wherein the permselective layer or second layer is a layer manufactured by seeded hydrothermal synthesis.
4. A composition as claimed in any of the preceding claims wherein the first and second layers are contiguous, intergrown layers having a thickness ranging from about 0.1 micrometers to about 100 micrometers and wherein 99% of the columnar molecular sieve crystals have at least one point between adjacent crystals that is less than or equal to 20Å.
5. A composition as claimed in any one of the preceding claims wherein the first and second molecular sieve layers are selected from the group consisting of silicalite, ZSM-5 zeolite, zeolite X, zeolite Y, and mixtures thereof.
6. A composition as claimed in any one of the preceding claims which further comprises a support in contact with the first molecular sieve layer.

7. A composition as claimed in any of the preceding claims wherein the second layer and first layer are epitaxial.
8. A composition as claimed in any one of the preceding claims wherein the composition further comprises an intermediate layer situated between the substrate and the first molecular sieve layer, the intermediate layer comprising nanocrystalline or colloidal-sized molecular sieves having interstices of about 20 to about 2,000 Å.
9. A composition as claimed in any one of the preceding claims which further comprises an mesoporous intermediate layer situated between the first and the second molecular sieve layers, the intermediate layer comprising nanocrystalline or colloidal-sized molecular sieves having interstices of about 20 to about 2,000 Å.
10. A molecular sieve membrane composite composition comprising:
 - a) a permselective layer of dense, columnar, polycrystalline molecular sieve material deposited on a substrate, and
 - b) a catalytically active region which is not in direct contact with the permselective layer.
11. A composition as claimed in claim 10 wherein the molecular sieve layer is independently selected contiguous, intergrown, polycrystalline molecular sieve ranging in thickness from about 0.1 to about 100 micrometers, and wherein the substrate is selected from the group consisting of stainless steel and alumina substrates, and wherein the catalytic functionality in the catalytically active region is a xylene isomerization catalyst.

12. The composition of claim 11 wherein the molecular sieve layer is selected from the group consisting of molecular sieve X, molecular sieve Y, ZSM-5 molecular sieve, silicalite, and mixtures thereof.
13. The composition of claim 12 further comprising a selectivity-enhancing coating capable of obstructing about 50% of the dense layer's pore openings and increasing the composition's mass transfer resistance by a factor ranging from about 1 to about 5 and selected from the group of permeable coatings, impermeable coating, and mixtures thereof.
14. A process for the manufacture of a molecular sieve composite composition comprising:
 - a) A permselective layer of dense, columnar, polycrystalline molecular material, and
 - b) a second independently selected layer of polycrystalline molecular sieve material, the second layer having a surface in contact with a surface of the permselective layer;

which process comprises deposition of the second layer prior to calcination of the first layer.

15. A process for the manufacture of a composite according to claims 1 to 9 in which process catalytic functionality or a precursor thereof is added to the synthesis process for deposition of the first layer after commencement of the synthesis, and the resultant catalytic region constituting the second molecular sieve layer.



Application No: GB 9915442.9
Claims searched: 1-9, 14-15

Examiner: Dr Albert Mthupha
Date of search: 25 November 1999

Patents Act 1977 Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK CI (Ed.Q): B1X; C1A (ACC)

Int CI (Ed.6): B01D (71/02)

Other: ONLINE: EPODOC, JAPIO, WPI.

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X	WO 97/25129 A1 EXXON, see page 7 line 20-page 8 line 25, page 14 lines 5-21, page 15 line 3-page 16 line 11.	1, 5, 6.
X	WO 96/01683 A1 EXXON, see page 2 lines 2-17, 25-26, page 5 lines 14-28, page 6 lines 1-16, page 7 line 24-29.	1, 2, 3, 5, 6.
X	WPI Abstract Accession No. 1998-182373 & JP 100036114 A (FINE CERAMICS), see abstract.	1, 5, 6.
X	WPI Abstract Accession No. 1998-182372 & JP 100036113 A (FINE CERAMICS), see abstract.	1, 5, 6.

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

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